

AD A046575

OFFICE OF NAVAL RESEARCH

15

Contract N00014-75-C-1179

9

Task No. NR 056-607

TECHNICAL REPORT, NO. 16

14

TR-16

6

CHARGE-TRANSFER INTERACTIONS BETWEEN
TRANSITION METAL HEXAFLUORIDES AND XENON.

by

10

J. D./Webb E. R./Bernstein

Prepared for Publication

in the

Journal of the American Chemical Society

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

11

October 1977

1/p.

DDC
RECEIVED
NOV 17 1977
E

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

Approved for Public Release; Distribution Unlimited.

AD No. _____
DDC FILE COPY

1412
404 992

4E

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DD FORM 1473
1 JAN 73

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

II. EXPERIMENTAL

Handling of hexafluorides has been previously described.¹ Research grade Xenon and Krypton (Linde) were used and were further purified by distillation to remove any traces of H_2O , a very serious impurity for the hexafluorides.

Crystals were grown from the melt by suspending the sample cell a few centimeters above the surface of liquid nitrogen in a closed dewar. Although crystals grown this rapidly (~20 min.) are certainly not high quality single crystals, they are of adequate quality to allow spectra to be taken. Visible and near UV absorption spectra were taken on a McPherson 285 monochromator with photoelectric detection. Near IR spectra were obtained on a McPherson 2051 with a 77K InAs (Texas Instruments) detector. Some preliminary spectra were also obtained on a Cary 17.

III. THEORY

The theory of CT transitions and complexes is well known⁴ and will be outlined only briefly here. For 1:n complexes (in this case n is either 12Xe or 1Xe), the energy of the CT transition is:

$$h\nu_{CT} = I_d - E_a + (G_1 - n'G_0) + (X_1 - n'X_0) \quad (1)$$

in which

I_d = Ionization potential of the donor D (Xe).

E_a = Electron affinity of the acceptor A (MF_6).

G_1 = "Normal" interaction of D^+ and A^- , specifically neglecting the CT interactions.

G_0 = "Normal" interaction of D and A.

X_1 = Additional interaction between D^+ and A^- due to proximity of D-A configuration.

X_0 = Additional interaction between D and A due to proximity of the D^+A^- configuration.

n = Number of donors in the complex.

n' = In the limit of weak complexes, $n' = n$. For stronger complexes $n' < n$ due to saturation effects.⁵

X_0 can be approximated by second order perturbation theory, as

$$X_0 \approx - \frac{\beta_0^2}{\Delta} \quad (2)$$

for which

$$\Delta = I_d - E_a + (G_1 - n'G_0)$$

$$\beta_0 = \langle \psi(D,A) | \hat{H}_0 | \psi(D^+,A^-) \rangle.$$

For the purpose of estimating electron affinities, the following approxi-

mate equation is useful:

$$h\nu_{CT} = I_d - E_a + G_1. \quad (3)$$

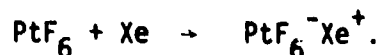
Location and character of excited electronic states of the donor and acceptor are of importance in more detailed considerations. The excited electronic states of Xe are so high in energy as to have a negligible effect in this regard and will be ignored here. The onset of intramolecular CT transitions for the hexafluorides is given in Table 1. The lowest energy ligand-field states of IrF_6 are shown in Figure 1. Note that in the above considerations solvent effects have been neglected.

IV. RESULTS

The onset frequencies of the intermolecular CT transition for 1/2% MF_6/Xe ($\lambda = 1$ cm) are listed in Table 1. The observed transitions are found to be broad ($>10,000$ cm^{-1}) featureless bands, as expected of a CT transition. The frequencies of the near IR transitions of 0.1% IrF_6/Xe ($\lambda = 1$ cm) are given in Table 2; a comparison of IrF_6/Xe data and neat IrF_6 is given in Table 3. The intensities of the near IR transitions of IrF_6/Xe are estimated to be enhanced by two orders of magnitude over those of neat IrF_6 . The band widths are increased by an order of magnitude over the observed band widths in neat IrF_6 . Near IR and visible spectra of gas phase 1/2% IrF_6/Xe (10 torr-liter Xe, $V = 10$ ml, $T = 300\text{K}$, $\lambda = 1$ cm) and solid 0.01% IrF_6/Kr ($\lambda = 1$ cm) show only the intramolecular CT transition at $20,000$ cm^{-1} characteristic of IrF_6 . Freezing the yellow gas phase IrF_6/Xe mixture in liquid nitrogen gives an opaque-purple solid; warming the sample to the melting point of Xe gives an opaque-purple liquid which upon warming evaporates, leaving yellow solid IrF_6 . With the evaporation of IrF_6 , a pale yellow gas obtains, leaving no residue behind.

V. DISCUSSION

Plausibility of the intermolecular CT transition hypothesis ($\text{MF}_6 + \text{Xe} \xrightarrow{h\nu} [\text{MF}_6^- \text{Xe}^+]$) can be easily demonstrated. PtF_6 is known to chemically react with Xe,⁶ the first step in the reaction being



Since PtF_6 has a higher electron affinity (215 kcal/mole⁷) than the hexafluorides studied here, it is not unreasonable to suspect that the $\text{MF}_6^- \text{Xe}^+$ electronic configuration would be an excited state rather than the ground state as in PtF_6/Xe . A rough calculation can be used to demonstrate this point quite adequately. The frequency of the CT transition in IrF_6/Xe using Eq. (3) with $I_d = 281$ kcal/mole, $E_a(\text{IrF}_6) \approx 136$ kcal/mole, $G_1 \approx -70$ kcal/mole, is found to be $h\nu_{\text{CT}} \leq 26,000 \text{ cm}^{-1}$.

Experimental verification of the CT transition hypothesis is given in Table 1. This data indicates that $E_a(\text{IrF}_6) > E_a(\text{MoF}_6) > E_a(\text{WF}_6)$ which agrees with the expected trends.⁶ Estimates of the electron affinities of MF_6 are made in Table 1. The best procedure for estimating these values seems to be to use $E_a(\text{WF}_6)$ as determined by the collisional ionization method⁸ and to estimate the others through the difference in the onset frequency of the intermolecular CT transition. The main source of uncertainty in this method is neglect of the interaction of the $\text{MF}_6^- \text{Xe}^+$ electronic configuration with the ground (MF_6Xe) and locally-excited (MF_6^*Xe) configurations. The latter might be more significant for IrF_6/Xe for which the CT transition occurs in the midst of the low-lying IrF_6 ligand field transitions (see Figure 1) and $\sim 10,000 \text{ cm}^{-1}$ from the intramolecular CT band of IrF_6 .

Since CT transitions often imply the formation of a CT complex, it is of

interest to determine if the $\text{MF}_6\text{-Xe}$ system forms such complexes. The CT transition in IrF_6/Xe is the closest to the ground state; thus, it is expected that the $\text{IrF}_6\text{-Xe}$ complex would be the most stable. The usual approach for determining stability of such complexes employs the method of Benesi and Hildebrand⁴ to find the equilibrium constant for complex formation. However, the near IR data obtained for solid IrF_6/Xe (Tables 2 and 3) and the near IR-visible data for gas phase IrF_6/Xe allow a simpler, though perhaps more approximate, alternative method to be utilized.

The fact that there is no evidence of the $\text{IrF}_6\text{-Xe}$ complex in the room temperature vapor indicates that the 1:1 complex is not strongly bound. The observed frequency shifts, increased linewidths (see Table 3), and intensity enhancements in the 0.1% IrF_6/Xe solid samples indicate that there is significant CT interaction between IrF_6 and Xe in the ground state. However, the solid state data pertain to an $\text{IrF}_6 \cdot 12\text{Xe}$ complex, whereas information on the 1:1 complex is of more intrinsic interest. Eq. (1) and the assumption that the complex is weak enough to allow n' to be set equal to 12 provides an approximate relationship between the 1:12 and the 1:1 complexes.

The stabilization energy of the ground state [$12\text{X}_0(\text{r}_8(^4\text{A}_2))$] of the $\text{IrF}_6 \cdot 12\text{Xe}$ complex can be estimated by assuming that Eq. (2) can be applied to the frequency shift data for the $\text{r}_8(^2\text{T}_1)$ state to find $\beta_0(\text{r}_8(^2\text{T}_1))$, and that $\beta_0(\text{r}_8(^4\text{A}_2))$ is roughly the same since both states stem from the $(\text{t}_{2\text{g}})^3$ configuration. These considerations lead to a value for $12\text{X}_0(\text{r}_8(^4\text{A}_2))$ of -300 cm^{-1} . The stabilization energy of the ground state $\text{X}_0(\text{r}_8(^4\text{A}_2))$ of the 1:1 complex is then -25 cm^{-1} . One would certainly expect this to be a lower limit since saturation effects⁵ have not been taken into account. The original assumption that the ground state complex is weak thus appears well justified.

The general picture that emerges for these weak charge transfer complexes

between Xe and MF_6 molecules is then as follows. The ground state is neutral probably with a shallow broad potential minimum somewhere near $r^\circ \sim 4\text{\AA}$, the Xe-Xe approximate distance in a crystal lattice or a liquid. It is possible that there are a few vibrational quanta in this well but this is not a necessary condition imposed by our data. The excited state potential well is much deeper, more narrow, and the potential minimum is such that $r^*(\text{MF}_6^-\text{Xe}^+) < r^\circ(\text{MF}_6\text{Xe})$. These considerations also account nicely for the very broad ($>10,000\text{ cm}^{-1}$) Franck-Condon envelope observed for the CT transitions in all systems.

VI. CONCLUSION

The new electronic transitions which appear when certain transition metal hexafluorides are dissolved in liquid Xenon can be assigned as intermolecular charge-transfer transitions. The concomitant charge-transfer complexes are weakly bound.

REFERENCES

1. E. R. Bernstein and G. R. Meredith, J. Chem. Phys. 64, 375 (1976).
2. E. R. Bernstein and J. D. Webb, Mol. Phys. __, __ (1977) and E. R. Bernstein, G. R. Meredith and J. D. Webb, Mol. Phys. __, __ (1977).
3. P. R. Hammond, J. Chem. Soc. (London) A1971, 3826 and references to earlier work therein.
4. R. S. Mulliken, W. B. Person, "Molecular Complexes, a Lecture and Reprint Volume", (Wiley, New York, 1969).
5. R. S. Mulliken, J.A.C.S. 64, 811 (1952).
6. N. Bartlett, Angew. Chem. Internat. Edit. 7, 433 (1968).
7. N. Bartlett as quoted by: R. N. Compton, J. Chem. Phys. 66, 4478 (1977).
8. C. D. Cooper, R. N. Compton and P. W. Reinhardt, "Abstracts of Papers of the IXth International Conference on the Physics of Electronic and Atomic Collisions", edited by J. S. Risley and R. Geballe (University of Washington Press, Seattle, 1975), Vol. 2, p. 922.

Table 1. Onset frequency for inter- and intramolecular charge-transfer transitions [$\sigma_{CT}(MF_6/Xe)$, $\sigma_{CT}(MF_6)$] and estimated electron affinities (E_a) for MF_6 . A literature value for $E_a(WF_6)$ is used in conjunction with Eq. (3) to determine the other $E_a(MF_6)$ (see text).

MF_6	$\sigma_{CT}(MF_6/Xe)$ (cm^{-1})	$\sigma_{CT}(MF_6)$ (cm^{-1})	E_a (kcal/mole)
IrF_6	9,800	20,000	181
ReF_6	>22,000	22,000	<146
WF_6	36,600	52,000	(104) ^(a)
MoF_6	26,300	50,000	133
UF_6	>26,000	26,000	<134

(a) C. D. Cooper, R. N. Compton and P. W. Reinhardt, "Abstracts of Papers of the IXth International Conference on the Physics of Electronic and Atomic Collisions", edited by J. S. Risley and R. Geballe (University of Washington Press, Seattle, 1975), Vol. 2, p. 922.

Table 2. Observable near IR transitions of 0.1% IrF₆/Xe. Frequencies are determined to ± 1 cm⁻¹.

MF ₆	Vacuum Wavenumber (cm ⁻¹)	FWHH (cm ⁻¹)(a)	Assignment
IrF ₆	5724	205	Γ_8 (² T ₁)
	6016	168	Γ_8 (² T ₁) + b.v. (b)
	6404	-	Γ_8 (² T ₁) + s.v. (c)
	6641	-	Γ_8 (² T ₁) + b.v. + s.v.
	7814	203	Γ_8 (² E)
	8036	-	Γ_8 (² E) + b.v.
	8324	207	Γ_6 (² T ₁)
	8575	-	Γ_6 (² T ₁) + b.v.

(a) FWHH = full width at half height.

(b) b.v. = bending vibrations (ν_4 , ν_5 , ν_6).

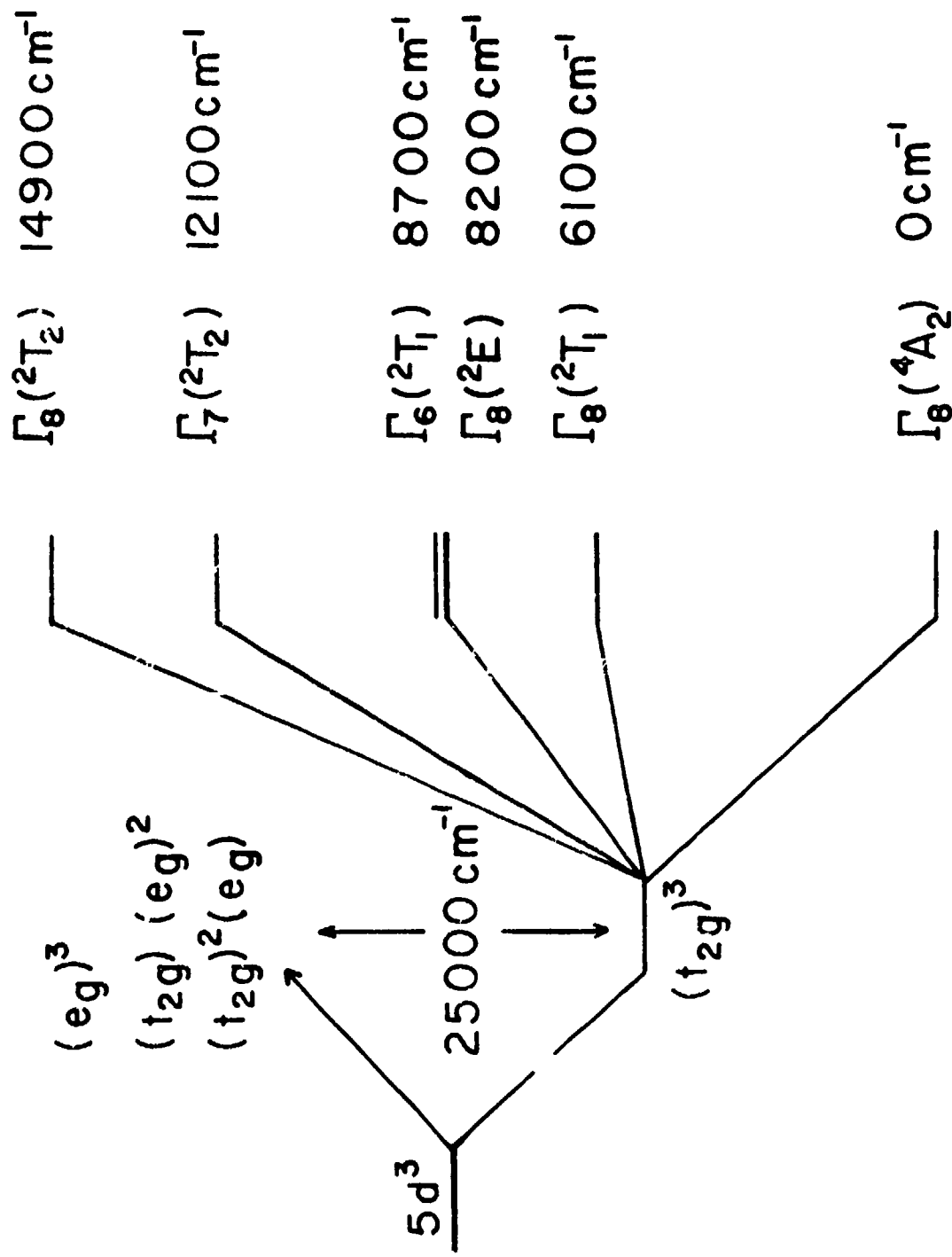
(c) s.v. = stretching vibrations (ν_1 , ν_2 , ν_3).

Table 3. Shifts in near IR origins between neat IrF₆ and 0.1% IrF₆/Xe.

	Neat IrF ₆ (cm ⁻¹)	0.1% IrF ₆ /Xe (cm ⁻¹)	Δ (cm ⁻¹)
Γ_8 (² T ₁)	6114	5724	-390
Γ_8 (² E)	8177	7814	-363
Γ_6 (² T ₁)	8701	8324	-377

Figure 1. Energy levels of IrF_6 . Rigorous symmetry labels (O_h^*) for each electronic state are given, along with the cubic Russell-Saunders state which correlates with the state for vanishing spin-orbit coupling. Since all the final states are gerade, the g label has been omitted in the right-hand column.

Energy Level Diagram of IrF_6



TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	6	U.S. Army Research Office P.O. Box 12211 Research Triangle Park, North Carolina 27709 Attn: CRD-AA-IP	
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	Commander Naval Undersea Research & Development Center San Diego, California 92132 Attn: Technical Library, Code 133	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
ONR Branch Office 1630 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Library, Code 2029 (ONRL)	6		
Technical Info. Div.	1		
Code 6100, 6170	1		
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1		
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1		

TECHNICAL REPORT DISTRIBUTION LIST

<u>No. Copies</u>		<u>No. Copies</u>
	Dr. M. A. El-Sayed University of California Department of Chemistry Los Angeles, California 90024	1
	Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	
	Dr. H. R. Bernstein Colorado State University Department of Chemistry Fort Collins, Colorado 80521	
	Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1
	Dr. G. Jones, II Boston University Department of Chemistry Boston, Massachusetts 02215	
	Dr. M. H. Chisholm Chemistry Department Princeton, New Jersey 08540	1
	Dr. J. R. MacDonald Code 6110 Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1
	Dr. G. R. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1
	Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah	1
	Dr. A. Adamson University of Southern California Department of Chemistry Los Angeles, California 90007	1
	Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1